

(12) UK Patent Application (19) GB (11) 2 112 388 A

(21) Application No 8235554
(22) Date of filing 14 Dec 1982
(30) Priority data
(31) 331856
(32) 17 Dec 1981
(33) United States of America (US)

(43) Application published 20 Jul 1983

(51) INT CL³
C07C 103/82

(52) Domestic classification
C2C 220 221 225 227
22Y 280 281 30Y 321 32Y
342 34Y 582 596 630
63X 80Y 815 AA KW
C3B 1D2C 1D3 1D6
1N6D1 1N6D4 1N6D5
1N6D8 1N6E E1
U1S 1346 1563 C2C C3B

(56) Documents cited
GB 1341417
GB 1238364

(58) Field of search
C2C
C3B

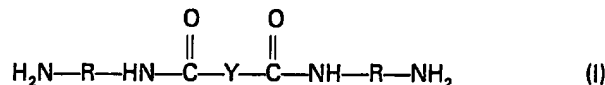
(71) Applicant
Ciba-Geigy AG,
(Switzerland),
Klybeckstrasse 141,
4002 Basle,
Switzerland

(72) Inventors
Jonas Weiss,
Raymond Seltzer

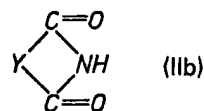
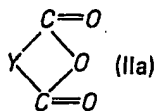
(74) Agent and/or address for service
Kenneth D. Sparrow,
Ciba-Geigy PLC,
Patent Department,
Tenax Road,
Trafford Park,
Manchester,
M17 1WT

(54) Carboxylic acid amides containing amino groups, and mixtures containing these amides and epoxy resins

(57) The compounds of the formula I



wherein Y is an aromatic, cycloaliphatic or aliphatic radical, to which the two carbonyl groups shown in the formula are bound in adjacent positions with respect to each other, and R is an arylene, aralkylene, cycloalkylene or cycloalkylalkylene group, can be produced by reaction of a compound of the formula IIa or IIb



with an amine of the formula III



They are used as latent curing agents for epoxy resins. Mixtures thereof with epoxy resins have excellent stability on storage.

GB 2 112 388 A

SPECIFICATION

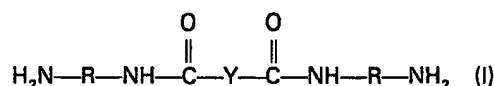
Carboxylic acid amides containing amino groups, and mixtures containing these amides and epoxy resins

5 The invention relates to special carboxylic acid amides containing amino groups, which amides are latent curing agents for epoxy resins, and to mixtures containing the said amides and epoxy resins.

10 Amines, amine derivatives and substituted amines as latent curing agents for epoxy resins are already known, for example from the U.S. Patent Specification No. 3,759,914. Latent curing agents prepared from acid anhydrides and linear aliphatic polyamines are described for example in the U.S. Patent Specification Nos. 3,261,882, 15 3,488,742 and 3,636,657. Reference is made in particular to the reaction product of phthalic anhydride and diethylenetriamine mentioned in these Patent Specifications.

20 The novel compounds according to the invention form a new class of latent curing agents having improved performance characteristics. In admixture with epoxy resins, they are stable for several months at room temperature and at 25 slightly higher temperature; but they cure in a relatively short time at elevated temperatures, for example in 10 to 60 minutes at 100 to 150°C, the epoxy resin to form a product having very 30 good properties, regardless of whether a freshly prepared mixture is used or a mixture which has been stored for several months. This result is surprising since the amides according to the invention contain free amino groups, of which it could have been expected that they would react at room temperature with epoxy groups. The improved performance characteristics are based in particular on better resistance to high 35 temperatures and to water, as well as on the higher glass transition temperature of the cured epoxy compounds. The mixtures of the amides according to the invention with epoxy resins can therefore be used for a wide range of purposes, for example in the preparation of prepreg 40 materials for the production and repair of composite structures.

The compounds according to the invention correspond to the formula I



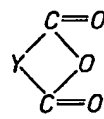
50 wherein Y is an aromatic, cycloaliphatic or aliphatic radical, to which the two carbonyl groups shown in the formula are bound in adjacent positions with respect to each other, and R is an arylene, aralkylene, cycloalkylene or cycloalkylalkylene group.

55 Preferably, Y in the formula I is the radical of phthalic acid, tetrahydrophthalic acid, methyl-tetrahydrophthalic acid hexahydrophthalic acid, succinic acid, dodecylsuccinic acid or maleic acid, 115

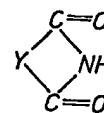
60 each unsubstituted or substituted by one or more lower alkyl groups having 1 to 4 C atoms, especially by one or more methyl groups; in particular Y is the radical of phthalic acid.

In the formula I, R is preferably the phenylene group, which can be substituted by alkyl groups having 1 to 4 C atoms, or it is the xylene group or the cyclohexylene group. Particularly suitable are the following compounds reduced by the 2 amino groups: m-xylenediamine, m-phenylenediamine, p,p'-methylenedianiline, bis-(p-amino- 65 phenyl)-sulfone, 1,2-diaminocyclohexane, 1,4-diaminocyclohexane, bis-(p-aminocyclohexyl)-methane, 1,3-bis-(aminomethyl)-cyclohexane, bis-(4-amino-3-methyl-cyclohexyl)-methane, 2,2- 70 bis-(4-aminocyclohexyl)-propane, 3,5,5-trimethyl-3-aminomethylcyclohexylamine (isophoronediamine) and 6-amino-1-(4-amino-phenyl)-1,3,3-trimethyl-indane. Especially preferred are the radicals of m-xylenediamine, 80 1,2-diaminocyclohexane, bis-(p-aminocyclohexyl)-methane and 1,3-bis-(aminomethyl)-cyclohexane.

The products of the formula I can be produced according to the invention by reaction of a 85 compound of the formula IIa or IIb

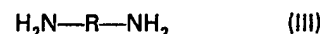


(IIb)



(IIa)

with an amine of the formula III



A condensation reaction occurs with cleavage 90 of the anhydride ring and imide ring, respectively, and formation of water and ammonia, respectively. There is advantageously used an excess of amine, namely, from a little over the stoichiometrically calculated amount up to a very considerable 95 excess, that is, up to a 100 molar-percentage excess. The reaction product is easily obtained by distilling off the excess amine under reduced pressure.

The reaction is advantageously performed 100 according to the general process described by Spring and Woods in the Journal of the Chemical Society, 1945, pp. 625—628. This is an aqueous process at temperatures of 20—50°C, which is best carried out by mixing the components at 105 30°C and performing the reaction at below 50°C. The reaction is usually performed at normal pressure; however, it can also be carried out under reduced pressure.

It is also possible to carry out the reaction by the method described in the U.S. Patent Specification No. 3,639,657, even though some of the thus produced curing agents are inclined to react much too fast with epoxy resins. In order to avoid this disadvantage, the process is modified 115 by performing the reaction in a dioxane solution,

and afterwards thoroughly purifying the product. The resulting products are in general vitreous solid substances having a low melting point.

- 5 The reaction of the acid anhydrides with the diamines does not always yield pure diamides; there are formed usually also monoamides. These can either be separated or be left in admixture with the diamides.

- The reaction products can be mixed by known mixing methods (stirring, kneading, rolling, and so forth) with an epoxy resin. The epoxy resins used are those which contain in the average molecule more than one epoxy group. Examples are: polyglycidyl ethers of polyhydric phenols, such as bisphenol A, F and S, cresol novolaks and phenol novolaks, glycidylated hydantoins, aromatic amines and aminophenols, polyglycidyl esters, and certain cycloaliphatic epoxy resins. Tetraglycidylated methylenedianiline is preferred.
- 20 Resins based on diglycidyl ethers of bisphenol A are likewise preferred for use in the fields of adhesives, coatings and filament windings.

- With regard to the epoxy resin the compounds according to the invention can be used in amounts which are 50 to 150%, preferably 100%, of the stoichiometric amount. When reacted with polyepoxides, for example diepoxides, at elevated temperatures, the compounds yield highly crosslinked products which are infusible and insoluble. With simultaneous shaping, by casting or moulding, shaped cast products, moulded articles or laminates can be produced. Furthermore, the resin/curing agent mixtures can be applied to substrates, and then cured in the form of a coating, a lacquer coating or adhesive bond.

- Such systems are frequently employed in the aerospace industry. They can be used to pre-impregnate fibres of various types, for example graphite, glass or Kevlar fibres, which can then be utilised as honeycomb skins. These systems are also suitable for producing laminates. The laminates can be prepared by known techniques, such as by moulding or by the autoclave method, and their layer thicknesses can vary within a wide range.

- There can be added to the mixtures of compounds of the formula I with epoxy resins further customary modifiers, such as extenders, fillers, reinforcing agents, pigments, dyes, organic solvents, fire-retarding substances, thixotropic agents, flow control agents and similar substances. Extenders, reinforcing agents and pigments which may be mentioned are: coal tar, bitumen, glass fibres, boron fibres, carbon fibres, cellulose, polyethylene powder, polypropylene powder, mica, asbestos, quartz powder, gypsum, antimony trioxide, montmorillonite derivatives (such as "Bentone"®), silica aerogel (Aerosil"®), lithopone, barite, titanium dioxide, carbon black, graphite, iron oxide, and metal powders, such as aluminium or iron powder. Flow control agents are for example: silicones, cellulose acetate butyrate, polyvinyl butyral, waxes, stearates, and similar products which are in part also used as

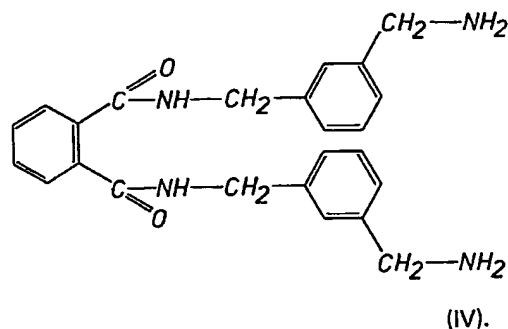
mould release agents.

- To adhesives containing an epoxy resin and a compound of the formula I, there can be added rubber substances, such as acrylonitrile-butadiene rubber containing carbonyl terminal groups, or modifying resins, such as triglycidylated p-aminophenol, accelerators, such as boron trifluoride monoethylamine complexes or imidazole complexes, or further curing agents, such as dicyandiamide.

The term 'parts' in the following Examples denotes parts by weight, and % is per cent by weight.

Example 1

- 80 To a solution (boiling at 110—120°C under nitrogen in reflux condenser) of m-xylylenediamine in dioxane is added dropwise a 20% solution of phthalic anhydride in dioxane, the amount added being such that to 1 mol of the anhydride there are 4 mols of the amine.
- 85 The addition is completed after 80 minutes, and the mixture is held at 110—120°C for 2 hours. Formed water and dioxane are removed in vacuo until the solution has become viscous. There are successively added hot heptane, toluene, hexane and ethyl ether until a solid substance in a yield of about 70% is obtained. The analysis (thin-layer chromatography, infra-red and NMR spectroscopy, amine titration, elementary analysis and electrical conductivity) shows that the product obtained is the amide of the formula IV (m.p. 124—127°C):



- The resulting product contains no salt-like compounds, such as amine carboxylate.

- A mixture of 100 parts of (IV) with 54 parts of tetraglycidylated methylenedianiline and 54 parts of triglycidylated p-aminophenol remains sufficiently storage-stable for 4 months at room temperature.

Example 2

- By the process described in J. Chem. Soc., 1945, pp. 625—628, bis-(p-aminocyclohexyl)-methane is reacted in an aqueous medium with phthalimide to give bis-(p-aminocyclohexyl)-methane phthalamide, the procedure being such that there is added to an aqueous emulsion of the amine, produced by vigorous stirring, within 10 minutes at room temperature, finely ground phthalimide in an amount of 1 mol to 2.4 mols of

amine; the mixture is then stirred for a further 40 minutes, subsequently poured into a separating funnel, and extracted with chloroform. The extract is dried over magnesium sulfate, filtered and freed from chloroform. The product is afterwards washed with hexane and then with anhydrous ethyl ether; the washing agent residues are distilled off in a vacuum oven.

A glassy product is obtained in a yield of 28% with a melting range of 75 to 90°C. The analysis (NMR spectrum) shows a reaction product consisting of 2 mols of amine with one mol of imide.

Example 3

In the same manner as that described in Example 2, phthalimide is reacted with 1,3-bis-(aminomethyl)-cyclohexane to obtain a glassy product having a melting range of 54—66°C. According to IR and NMR spectra, the product is the diamide consisting of 1 molecule of phthalic acid and 2 molecules of the amine.

Example 1

In the manner described in Example 2, phthalimide is reacted with 1,2-diaminocyclohexane. A slightly brownish coloured product having a melting range of 69—75°C is obtained. The IR and NMR spectra show that the product is a diamide consisting of 1 molecule of phthalic acid and 2 molecules of the amine.

Example 5

The same product as in Example 4 is obtained also by reaction of phthalic anhydride with 1,2-diaminocyclohexane, whereby 2 mols of the amine are reacted with 1 mol of the anhydride for 45 minutes at 125°C, without the use of a solvent.

In the same manner as described in the Examples, it is possible to react also the other aforementioned amines with the corresponding imides or acid anhydrides to obtain compounds according to the invention.

Application examples

A homogeneous paste consisting of 100 parts of the compound according to Example 1 as curing agent, 54 parts of tetraglycidylated methylenedianiline (Araldit® MY 720) and 54 parts of triglycidylated p-aminophenol (Araldit® 0510) is subjected to a differential thermo-analysis (DSC: differential scanning calorimetry). It is found that at 114°C a heat of reaction of 293.16 kJ per mol is developed. This value shows that the reaction is virtually complete at temperatures below 150°C. The mixture is stored at room temperature, and is examined at regular intervals of time to determine its stability in storage. It is shown that the heat of reaction during 11 weeks decreases only slightly (from 293 kJ to 279 kJ/mol, which is 96.5% of the initial value). It is still 84% of its initial value after 16 weeks. Colour and flow properties are practically unchanged after five months, and all

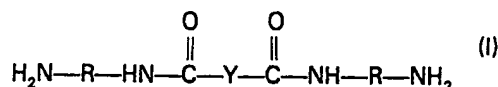
tests show a shelf life at room temperature of four months.

The mixture is moulded in a moulding press for 30 minutes at 150°C under a pressure of 412 MPa to obtain round discs of 2.5 cm diameter. After a postcuring at 150°C, the glass transition temperature is determined as being 120 to 130°C (DCS method). The water adsorption at 71°C with 95% relative humidity is 5.5%.

Similar values are obtained with the use of compounds according to Examples 2 to 5 and epoxy resin mixtures according to this Example, or epoxy resins based on bisphenol-A or cycloaliphatic epoxy resins.

75 Claims

1. A compound of the formula I



wherein Y is an aromatic, cycloaliphatic or aliphatic radical, to which the two carbonyl groups shown in the formula are bound in adjacent positions with respect to each other, and R is an arylene, aralkylene, cycloalkylene or cycloalkylalkylene group.

2. A compound according to Claim 1, wherein Y in the formula I is the radical of phthalic acid, tetra- or hexahydrophthalic acid, succinic acid, dodecylsuccinic acid or maleic acid.

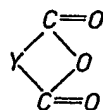
3. A compound according to Claim 1, wherein R in the formula I is the m-xylylene group, 1,2- or 1,4-cyclohexylene group, bis-(cyclohexylene)-methane group, 1,3- or 1,4-bis-methylene-cyclohexane group, bis-(3-methyl-cyclohex-1,4-ylene-methane group or 3,5,5-trimethyl-3-methylene-cyclohexyl group.

4. A compound according to Claim 1, wherein R is the m- or p-phenylene group, the p,p'-diphenylmethane group, the bis(p-phenyl)-sulfone group or the 1-(p-phenylene-1,3,3-trimethyl-indan-6-yl group.

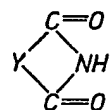
5. A compound according to Claims 2 and 3 or 2 and 4.

6. A compound of formula I substantially as described with reference to any of Examples 1 to 5.

7. A process for producing a compound of the formula I according to any one of claims 1 to 6, which process comprises reacting a compound of the formula IIa or IIb

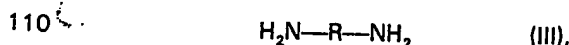


(IIa)



(IIb)

, with a compound of formula III



wherein Y and R have the meanings defined in Claims 1 to 5.

8. A process of producing a compound of formula I substantially as described with reference to any of Examples 1 to 5.

5 9. A compound of formula I when produced by a process claimed in claim 7 or 8.

10. A curable mixture which contains a

compound according to any one of Claims 1 to 6 and a polyepoxy compound.

11. A curable mixture according to claim 10 substantially as described with reference to any of the Application Examples.